2. The anhydro compounds obtained are colored in such a way as to indicate the possibility of quinoid structure.
3. β-Resorcylic acid can be mercurated in alkaline solution to give a dimercurated product.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE THERMAL DECOMPOSITION OF GASEOUS GERMANIUM TETRAETHYL

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In connection with the modern theory of the mechanism of gaseous reactions it probably would be very helpful to study the kinetics of decomposition of a series of molecules which present a stepwise gradation of structure and stability. With this in mind we have begun an investigation of the thermal decompositions of the tetra-alkyls (such as the tetramethyls and tetraethyls) of carbon, silicon, germanium, tin and lead. This family of compounds presents a considerable variety of sizes of the central atom, a great difference of bonding forces with which the outlying groups are bound to the central atom, and affords the possibility of examining related molecules of various degrees of complexity. Preliminary study shows that the temperatures of appreciable decomposition extend over a wide range, from about 220° for lead tetraethyl to about 650° for silicon tetramethyl, and that in at least two cases, germanium tetraethyl and lead tetraethyl, and probably in all of the other cases, the decomposition is predominantly homogeneous and unimolecular. The present paper is an account of the behavior of germanium tetraethyl. Data for the other compounds will be presented in later papers.

The thermal decomposition of gaseous germanium tetraethyl in the range 420–450° is a reaction about 98% homogeneous, and unimolecular down to pressures of about 8 cm. During the course of the decomposition, metallic germanium is deposited as a semi-mirror, or as what amounts to a sputtered film, on the walls of the reaction vessel, and it seems natural to represent the primary reaction as

$$Ge(C_2H_5)_4 \longrightarrow Ge + 4C_2H_5$$

(It must be admitted that this is only a suggested manner of decomposition, and that there is not enough evidence to justify setting up a detailed reaction mechanism. A similar formation of free methyl[2] groups seems to be well established in the decomposition of lead tetramethyl.) The free ethyl groups might then be supposed virtually to unite to form normal bu-

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[2] Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

tane, and indeed in a preliminary study of the decomposition of lead tetraethyl (250°), this seems to be essentially what occurs; but in the case of germanium tetraethyl, which decomposes at a temperature almost 200° higher than lead tetraethyl, it is not likely that much actual butane would be formed. Hague and Wheeler[3] noticed slow decomposition of butane at about 435°, and Hurd and Spence[4a] found some decomposition even at 400°. The ethyl groups sloughed off from the germanium may react to give gaseous products very much like the products which Hurd and Spence found for the pyrolysis of *n*-butane. Our ethyl groups yield 60–70% ethane and ethylene, a proportion which would be obtained if the butane molecules split in the middle, and followed predominantly Equation 2 of Hurd and Spence.[4b] A more detailed account of the decomposition products will be presented in Table V.

Experimental

The course of the decomposition of germanium tetraethyl was followed by measurement of the change of pressure in a reaction vessel. Because of the low vapor pressure of germanium tetraethyl at room temperature, glass membrane manometers of the null type described by Jackson[5] and Gibson[6] were employed. A combination mercury-piston mercury manometer was used for adjusting and measuring the higher air pressures outside the glass membrane, and an ethyl phthalate manometer for measuring the lower pressures (1–2 cm.).

Both pyrex and quartz membranes and reaction chambers (of about 10–15 cc. capacity) were constructed. At 440° even the stiffer pyrex membranes had a slight tendency to soften, although the subsequent change in zero point was not enough to affect the calculations to any great extent. However, to eliminate possible error from this source, clear fused quartz reaction chambers were used in practically all cases. The quartz membrane manometers were made of various degrees of sensitivity, depending on the pressures at which they were intended to serve. A few were estimated to have an extreme sensitivity of about 0.002 mm.

Constant temperature was maintained, within 0.1–0.2°, with a sulfur-bath boiling under the required pressure, generally for convenience at atmospheric pressure. The temperature was measured with a carefully calibrated chromel–alumel thermocouple placed alongside the reaction chamber at its mid-portion.

Samples of germanium tetraethyl were very kindly donated by Professor L. M. Dennis of Cornell University, Professor C. A. Kraus of Brown University, and Mr. Thomas Midgley, Jr.

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[3] Hague and Wheeler, *Fuel Science Practice*, 8, 560 (1929).

[4] (a) Hurd and Spence, This Journal, 51, 3353 (1929); (b) p. 3358.

[5] Jackson, *J. Chem. Soc.*, 99, 1066 (1911).

[6] Gibson, *Proc. Roy. Soc. Edinburgh*, 33, 1 (1912).

Briefly the procedure in making a run was as follows. A small amount of liquid germanium tetraethyl was sealed up in a small glass bulb with minute capillary ends in such a way that the bulb was filled and only an extremely small quantity of air was left in the capillary ends. This was an important precaution since small amounts of oxygen were found to increase the rate of decomposition quite appreciably. The reaction chamber was connected to a diffusion pump system by a short length of suction tubing, after a bulb of germanium tetraethyl had been placed in the tube a short distance from the chamber. The air pressure was reduced to about 0.001 mm., and during this evacuation the chamber was heated for about fifteen minutes with a blast lamp to remove adsorbed gases. The chamber, was then allowed to cool, the bulb rolled down into the chamber and the latter sealed off. The chamber was preheated in an electric furnace to a temperature about 100° below the temperature of appreciable decomposition, and from the pressure of the germanium tetraethyl at this temperature the initial pressure at the temperature of the decomposition run was calculated by means of Charles' law. The reaction chamber was quickly withdrawn from the furnace, thrust into the sulfur bath, clamped fast in a vertical position and a microscope focused on the edge of the membrane manometer pointer when it was in its zero position. Simultaneous readings of pressure and time were taken at one- to two-minute intervals during the first three-quarters of the decomposition, and at longer intervals during the remainder. The data for a typical run at 440.9° are given in Table I.

TABLE I

DATA AND VELOCITY CONSTANT AT 440.9°

Time, minutes	Pressure, cm.	$p_\infty - p$	Velocity constant, k	Time, minutes	Pressure, cm.	$p_\infty - p$	Velocity constant, k
0	30.74	77.16	.....	15.60	68.66	39.24	0.0492
2.45	33.97	73.93	.....	17.25	71.56	36.34	.0465
3.85	37.87	70.03	0.0389	19.12	74.50	33.40	.0432
5.35	42.27	65.63	.0432	26.30	82.80	25.10	....
6.40	45.58	62.32	.0493	29.97	85.62	22.28	.0325
7.75	49.75	58.15	.0512	49.10	94.40	13.50	....
9.44	54.65	53.25	.0521	64.75	97.90	10.00	.0192
10.73	57.98	49.92	.0501	187	106.20	1.70	....
12.65	62.62	45.28	.0509	225	107.10	0.80	....
14.17	65.80	42.10	.0479	267	107.90	.00	....

Column 3 gives the differences between the final pressure and the pressures at the various time intervals. After the first five minutes the velocity constant, k, calculated between successive time intervals by the usual unimolecular equation, assumes a fairly constant value and remains fairly constant until the reaction is about 50% completed, and then falls off considerably.

The fact that the decomposition is almost wholly homogeneous is demonstrated by the data presented in Table II.

TABLE II

HOMOGENEITY OF THE REACTION IN QUARTZ

Run	Temp., °C.	p_{initial} (cm.)	k	k (442°)	Surface ratio
Average	...	..	....	0.0505	1
75	442.3	12.7	0.0550	.0544	10
115	442.2	24.2	.095	.094	40–50
204	441.1	29.5	.095	.099	40–50
206	441.8	35.9	.090	.091	40–50

In Column 5 the velocity constants are corrected to 442°. Since an increase in the surface to volume ratio of 40–50 times does not quite double the velocity constant, it follows that the reaction cannot be more than about 2% heterogeneous. The reproducibility of results from run to run argues for a largely homogeneous reaction. The reaction was also homogeneous in pyrex.

That the decomposition is kinetically unimolecular is shown by the very constant values for the time of half change, $t_{1/2}$, in Col. 6, and by the good

TABLE III

DATA SHOWING UNIMOLECULAR CHARACTER OF THE REACTION

Run	Temp., °C.	Vessel	p_0, cm.	p_∞/p_0	$t_{1/2}$, minutes	k	k (442°)
190	441.6	P	46.5	3.43	16.5	0.048	0.049
198	441.5	P	42.9	3.37	17.0	.052	.054
132	441.7	Q	36.1	3.21	13.5	.056	.057
89	442.3	Q	36.3	3.49	16.5	.048	.047
91	442.4	Q	34.0	3.61	17.0	.050	.049
178	442.0	P	33.0	3.64	12.5	.057	.057
194	440.9	P	30.7	3.51	16.0	.051	.054
85	441.8	Q	30.9	3.56	17.0	.046	.047
43	441.2	P	28.5	3.46	16.5	.051	.053
69	441.6	Q	26.6	3.63	15.0	.054	.055
45	439.9	P	26.2	3.20	16.8	.051	.057
87	441.9	Q	25.4	3.66	15.0	.0475	.048
63	441.3	P	24.6	3.58	17.0	.047	.049
67	441.8	Q	24.6	3.70	17.0	.0495	.050
136	441.4	Q	22.6	3.63	15.0	.051	.0525
83	441.8	Q	21.0	3.61	16.3	.050	.0505
59	442.1	P	19.3	3.20	16.5	.046	.046
65	440.9	Q	18.5	3.90	14.0	.057	.060
41	440.6	P	16.3	3.46	16.5	.0525	.056
134	441.9	Q	15.2	3.76	17.5	.048	.048
71	442.1	Q	13.2	3.80	17.0	.046	.046
79	442.1	Q	13.1	3.54	16.0	.052	.052
39	441.2	P	11.0	3.44	15.0	.052	.054
254	441.2	Q	8.8	3.81	16.5	.053	.055
250	441.0	Q	3.3	4.59	38	.017	.018
252	441.3	Q	1.94	4.89	41	.0135	.0140
248	440.2	Q	1.7	4.98	40	.015	.0164

agreement among the velocity constants of the various runs, indicated in Col. 8 of Table III.

Column 3 indicates the nature of the reaction chamber, pyrex or quartz, Col. 4 the initial pressure, and Col. 5 the ratio of final to initial pressure.

The variation of the velocity constant with temperature is shown in Table IV.

TABLE IV

TEMPERATURE COEFFICIENT DATA

Init. press., cm.	Temp., °C.	Velocity constant, k
Average	442	0.0505
22.7	431	.031
22.2	431.1	.030
26.9	430.6	.031
33.8	419.5	.0153
16.4	419.1	.0142

The velocity constant as a function of temperature may be expressed approximately by the equation

$$\ln k = 32.88 - 51{,}000/RT$$

The energy of activation of this reaction is about 51,000 with a possible error of several thousand calories.

Discussion of Results

Reference to the last three runs of Table III shows that the velocity constant begins to drop off appreciably at low pressures. At a partial pressure of germanium tetraethyl of about 7 cm. the velocity constant is about 0.040. We have estimated the effective diameter of a germanium tetraethyl molecule to be about 7 Å. from the critical density, by using Herzog's[7] empirical equation; and also roughly from the average shadow area[8] of a model of the molecule. From these data we have calculated that z, the total number of collisions per cc. per second, is 6×10^{26} and that the number of molecules reacting per cc. per second is 6.3×10^{14}. Then from the usual equation[9]

$$k\left(\begin{matrix}\text{molecules}\\ \text{reacting}\end{matrix}/\text{cc./sec.}\right) = 2.5\, z e^{-\left[\frac{E+\left(\frac{1}{2}n-1\right)RT}{RT}\right]} \cdot \left[\frac{E+\left(\frac{1}{2}n-1\right)RT}{RT}\right]^{\frac{1}{2}n-1} \Bigg/ \left(\frac{1}{2}n-1\right)$$

we obtain a value between 8 and 10, for n the number of so-called active degrees of freedom, or the number of "square terms."

Although the velocity constant falls off at low pressures, the introduction of hydrogen at a pressure of 20 cm. into germanium tetraethyl at a pressure

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[7] Herzog, *Z. Electrochem.*, 15, 345 (1909).

[8] Mack, THIS JOURNAL, 47, 2468 (1925).

[9] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford, 1929, 2d ed., p. 155.

of 4.6 cm. failed to raise the value of the constant appreciably. Helium, argon and nitrogen at pressures of about 60 cm. were added to the germanium tetraethyl at about 25 cm. and at first the results seemed to indicate that these inert gases were raising the value of the velocity constant. However, careful analysis of the helium, argon and nitrogen showed the presence of oxygen to the extent of 0.1–0.2%, and since the presence of oxygen in concentrations as large as this in the germanium tetraethyl system increased the velocity constant (in blank determinations) to about the same extent as that found in the case of the inert gases, we concluded that the helium, argon and nitrogen themselves had in reality little, if any, effect on the velocity of the reaction. Our experience with the effect of oxygen in this system leads us to suggest that the increase in the velocity constant observed by Pease[10] and Durgan for the pyrolysis of butane and propane, in the presence of added nitrogen, may be explained by the presence of small quantities of oxygen.

Carbon dioxide, at pressures of 42.4 and 86.5 cm., in germanium tetraethyl at pressures of 21.7 and 8.2 cm., respectively, caused the velocity constant to fall off to 0.034 and 0.024. The lowering was approximately proportional to the partial pressure of the carbon dioxide. This behavior suggests that the activated germanium tetraethyl molecules are being robbed of energy of activation by collision with the carbon dioxide molecules, and indeed the observed falling value of the velocity constant with gradual accumulation of reaction products toward the latter part of the reaction is in line with the same idea.

When hydrogen was introduced into the system with germanium tetraethyl at ordinary pressures (15–25 cm.), the ratios of the final to initial pressures indicated that some of the hydrogen was disappearing in the reaction, and the amounts disappearing were roughly proportional to the pressure of the added hydrogen. Since hydrogen at pressures above about 25 cm. was lost in appreciable amounts by diffusion through quartz membranes of the type we were using, it was necessary to conduct these experiments in pyrex. Analysis of the products of the reaction showed undoubtedly that the disappearance of hydrogen in the reaction was due to the hydrogenation of unsaturated hydrocarbons, as Pease found in the case of ethylene–hydrogen mixtures,[11] although, in the present instance, as suggested below, it seems likely that the hydrogenation reaction occurs at the instant of germanium tetraethyl decomposition.

Analyses of the gaseous products of decomposition were carried out in a modified Bone–Wheeler apparatus. Special reaction vessels were constructed in order to facilitate the handling of the small volumes of gas, amounting to about 10 cc., available for analysis. When the decomposi-

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[10] Pease and Durgan, THIS JOURNAL, **52**, 1262 (1930).

[11] Pease, *ibid.*, **52**, 1185 (1930).

tion was completed, the chamber was cooled to room temperature and the pressure measured. This pressure, when calculated by Charles' law to the temperature of the decomposition, in nearly all cases checked fairly well with the final pressures actually measured, thus affording evidence that the amounts of high-boiling compounds were very small or zero. The chamber was then cooled to liquid-air temperatures and the vapor phase, consisting of hydrogen and methane, pumped off by means of a Töpler pump. The residue was warmed to room temperature, cooled in liquid air and the vapor phase pumped off again. As a rule very small amounts of gas were obtained from this second fractionation. By slow combustion analysis the amounts of hydrogen and methane in the original sample were obtained. The residual gas in the reaction chamber was pumped out and analyzed for saturated and unsaturated hydrocarbons. At first the unsaturation was estimated only as ethylene and higher olefins, according to Hague and Wheeler. In later analyses the higher olefins were separated into groups according to Hurd and Spence. Combustion of the saturated hydrocarbons gave the average carbon content per molecule, and showed the presence of practically nothing except ethane and propane. No great accuracy is claimed for the analysis, but on any given sample it is probably correct to within a few per cent. Typical analyses are given in Table V. It will be noted from the table that the total percentage of unsaturation is practically independent of the two methods, (a) and (b), employed, although the separation of the different groups of the unsaturated fraction according to the Hurd and Spence method (b), is undoubtedly more reliable.

TABLE V

ANALYSIS OF GASEOUS PRODUCTS

					Added hydrogen		
Run	168[a]	178[a]	194[b]	198[b]	170[a]	174[a]	182[a]
Hydrogen, %	11.6	10.6	10.6	11.5	11.0	11.0	11.0
Methane, %	12.2	9.9	7.5	9.5	14.8	15.5	15.0
Ethane, %	29.9	34.2	41.5	43.9	51.4	45.0	56.3
Propane, %	10.3	8.6	3.3	2.9	4.0	5.4	0.0
Ethylene, %	29.2	29.6	21.7	17.3	14.8	16.7	14.3
Propylene + butylene, %	...	...	12.7	12.9	...	...	...
Isobutylene, etc., %	...	...	1.6	1.7	...	...	...
Acetylenes. %	...	...	1.4	0.3	...	...	0.3
Higher olefins (propylene, etc.), %	6.9	9.8			3.8	6.1	2.8

[a] Hague and Wheeler method of analysis of unsaturation. [b] Hurd and Spence method.

Among the experiments in which hydrogen was added to the reaction system were three, namely, Runs 170, 174, 182, with the added hydrogen at a pressure of about 50 cm., which are tabulated above. In order to obtain a comparison between the composition of the product gases in these cases and the normal decompositions in the absence of added hydrogen, it was assumed as an approximation that about 11% of hydrogen would be formed in all of the decompositions, and the added hydrogen was not included in the listed percentage composition.

The data show clearly that in the presence of added hydrogen the decomposition yields a higher proportion of saturated hydrocarbons. Still, a large part of the unsaturation always remains. In addition, the times of half change, $t_{1/2}$, had about the same value as in the absence of added hydrogen. This indicates that the hydrogenation takes place simultaneously with the decomposition of the germanium tetraethyl molecule. and not in a later independent reaction. It seems probable that during the instant immediately following decomposition, while an unsaturated molecule (C_2H_5, C_2H_4, etc.), still has its share of the energy of activation from the decomposition, it is much more easily hydrogenated by collision with hydrogen than after the loss of this energy by collision with other molecules.

When the decomposition was carried out in the presence of *added* ethylene, part of the ethylene was found to disappear during the reaction. Probably there were two factors involved, hydrogenation and polymerization to the more stable butylene, as Pease found in the case of ethylene–hydrogen mixtures at this temperature. This polymerization, with large amounts of added ethylene, had the effect of raising the velocity constant during the first part, and of lowering it during the last part, of the reaction. This effect is to be expected since the calculation of the velocity constant involves the final pressure and since the polymerization lowers the ratio of final to initial pressure markedly. The polymerization of ethylene comes practically to a stop toward the later stages of a run, not only because of the decreasing partial pressure of the ethylene, but probably also because of the decreasing effect of the falling concentration of germanium tetraethyl on the polymerization. Taylor[12] and Jones have recently claimed that decomposition of metal alkyls induces ethylene polymerization.

In a *normal* run, in the absence of *added ethylene*, it seems that the velocity constant and the time of half change of the primary decompositions of germanium tetraethyl are unaffected by any reactions occurring among the product gases, if such reactions occur at all, or at least that these latter consecutive reactions must be rapid compared with the slower primary decomposition. Other considerations, as well, seem to justify the validity of using pressure measurements as a means of following the course of the primary decomposition.

The above analyses also show that the products vary slightly in proportion from run to run. This is also indicated by the variation in the values of the ratios of final to initial pressure in Table III. It is to be noted, though, that the absolute variations in the ratios of final to initial pressures

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[12] Taylor and Jones, This Journal, **52**, 1111 (1930).

are not to be taken too seriously, since there is one important source of error in the determination of these values. The final pressure was measured in the sulfur-bath; the initial pressure in an electric furnace. It was not always expedient to see that the chamber took exactly a vertical position in both cases. Hence the weight of the manometer pointer would cause error in each measurement which would be magnified in the ratio. Since the velocity constants were calculated from differences in pressure in the sulfur-bath, they are reliable in spite of the possible error in the absolute pressures.

Summary

The thermal decomposition of gaseous germanium tetraethyl in the temperature range 420–450° has been studied and has been found to be about 98% homogeneous, and unimolecular down to a pressure of about 8 cm.

At about 7 cm. the value of the velocity constant begins to fall off, but the addition of hydrogen gas to the reaction system does not raise the constant appreciably.

The energy of activation is about 51,000, with a possbile error of several thousand calories, and the velocity constant is given by the equation, $\ln k = 32.88 - 51{,}000/RT$. The number of active degrees of freedom calculated at the pressure where the velocity constant begins to fall off is between 8 and 10.

The reaction yields metallic germanium, and analysis of the gases from the decomposition shows essentially the products obtained by pyrolysis of butane. Added hydrogen and ethylene enter into hydrogenation and polymerization reactions in the gaseous system. Added carbon dioxide cuts down the velocity constant, but nitrogen, helium and argon have little, if any, effect.

It seems justifiable to measure the course of this decomposition by pressure changes, and the pressures have been measured with quartz and pyrex membrane manometers.

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